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PROPERTIES AND APPLICATIONS OF MOLECULAR FORCES

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ABSTRACT: The attractive forces between molecules can be obtained simply in approximate form on the basis of a dispersion curve alone, i.e., from purely optical data. In sharp contrast to the electrostatic and valence type forces previously considered, these forces derived from the dispersion curve actually show the characteristics of a general cohesion. This is an attractive force, comparable to gravitation, which exists between many molecules simultaneously and (at least approximately) remains constant. It is only on the basis of this superposability of molecular forces that it is possible to explain the parallelism which has often been observed between the van der Waals deviations of real gases, heats of vaporization, heats of absorption, and other manifestations of molecular forces; it places all of them on a common theoretical basis, which could not be provided by a consideration of electrostatic and valence-type force effect alone. After the van der Walls correction had been determined previously from the abovementioned optical data, it became possible to determine from these same data the heats of sublimation of molecular lattices (§4), heats of absorption of absorbed gases (§5) and dissociation energies of molecules held together by van der Waals forces (§ 6). The accuracy of the agreement remains strictly within the boundaries which are still imposed by the lack of accuracy in the available empirical data and a lack of knowledge of the repulsive forces.

INTRODUCTION

The phenomenological consideration of the gas laws, surface tension, absorption, condensation and similar phenomena long ago led to the assumption of a common molecular attractive force common /222* to all of these processes. Consequently, the most elementary molecular-theoretical treatment of these phenomena usually attributes to the individual molecules a sort of uniform, fixed, adhesive force. Studies of this type, which proceed on the basis of this extremely primitive viewpoint, seek to relate molecular attraction to the balance of our knowledge of the electrical structure of matter; they usually discuss the electrostatic effect of fixed or polarizable charges; here, however, they are faced with the difficulty that /223 electrostatic models, owing to the duality of positive and negative electricity, are in no position whatsoever to produce a common attraction like that of gravitational forces. Either we have the case that two bodies are attracted by a third, while quite different forces simultaneously exist between the first two bodies and are mostly repulsive forces, (on the other hand) if the forces are based on the displaceability of the charges, the force prevailing between two bodies is dependent on whether a similar third body is in the vicinity. In general, it is not justifiable to add together the forces which two isolated, freely movable systems of charges exert on one another, in a simple manner like the central forces of fixed force centers; for example, on this basis it is completely impossible to understand how the same forces which are created by deviations from the ideal gas laws according to the van der Waals theory can remain critical for the liquid state only to an approximate degree. Even the effects which are based on polarizability will arise mutually in the molecular structure of a liquid. In any case, the superposition of these forces requires a careful consideration of all details of their mutual spatial positions and orientations; they are anything but fixed superposable central forces.

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* Numbers in the margin indicate pagination in the original text.

In addition to these forces, which are based on static and possibly polarizable charge distributions, a discussion of molecular attraction also involves those effects which arise from the fact that a molecule in reality is not a static-elastic charge continuum, but contains an extraordinarily rapid, internal electron movement, whose time averages show the same charge structure which served as the basis of the previously discussed electrostatic considerations.

It has been shown that the mutual "short period disturbances" of precisely these rapid internal motions of the electrons give rise to attractive forces between two molecules, which in many cases form the principal component of the van der Waals attraction [1]. As shown in this paper, the potential of these forces can be given for great distances if the dispersion formula of the specific molecule is known. It is therefore a value which can be determined /224 in principle from optical measurements. We will show (§ 2) that these forces are basically different from all electrostatic and valence type forces in that they give rise to a general additive attraction and are therefore suitable, in the field of their applicability, for placing the many types of phenomena of molecular attraction on a very simple, common theoretical basis with the assumption of six superposable forces.

In the following, I would like to mention a few particularly appropriate applications of these forces which in no way claim to exhaust the subject.

§1. AN ELEMENTARY MOLECULAR MODEL

It will perhaps be useful to begin with a detailed discussion of an elementary and readily resoluable example to show how these molecular forces come about. As the simplest molecular model, we will consider a quasi-elastic dipole whose variable electrical moment is described by the vector $e\mathfrak{r}$, m and α are its mass and polarizability, and $\mathfrak{p}$ is the impulse which belongs to $\mathfrak{r}$. The Hamiltonian of the two molecules of this kind which are located at a fixed distance R from one another can then be broken down into three components: the kinetic energy, the potential (quasi-elastic) energy of the molecules individually, and the interaction potential of the molecules with one another, of which only the dipole component will be considered:

$$H=\frac{1}{2m}(\mathfrak{p}_1^2+\mathfrak{p}_2^2)+\frac{e^2}{2\alpha}(\mathfrak{r}_1^2+\mathfrak{r}_2^2)+\frac{e^2}{R^3}(x_1x_2+y_1y_2-2z_1z_2). \qquad (1)$$

Here x_1, y_1, z_1 are the components of $\mathfrak{r}_1$; x_2, y_2, z_2 are those of $\mathfrak{r}_2$; the origins of the coordinates are assumed to lie at the centers of gravity of the molecules, the axes of the system of coordinates are parallel to one another, and we must particularly imagine the z-axes to be oriented in the direction of the line connecting the centers of gravity of the molecules. If we write the generalized coordinates of the principal oscillations,

$$\left.\begin{aligned}\mathfrak{r}_+&=\frac{1}{\sqrt{2}}(\mathfrak{r}_1+\mathfrak{r}_2)\\ \mathfrak{r}_-&=\frac{1}{\sqrt{2}}(\mathfrak{r}_1-\mathfrak{r}_2)\end{aligned}\right| \qquad \left.\begin{aligned}\mathfrak{p}_+&=\frac{1}{\sqrt{2}}(\mathfrak{p}_1+\mathfrak{p}_2)\\ \mathfrak{p}_-&=\frac{1}{\sqrt{2}}(\mathfrak{p}_1-\mathfrak{p}_2)\end{aligned}\right| \qquad (2a)$$

the Hamiltonian then breaks down into a series of six decoupled oscillators as follows: /225

$$H=\frac{1}{2m}(\mathfrak{p}_+^2+\mathfrak{p}_-^2)+\frac{e^2}{2\alpha}(\mathfrak{r}_+^2+\mathfrak{r}_-^2)+\frac{e^2}{2R^3}(x_+^2+y_+^2-2z_+^2-x_-^2-y_-^2+2z_-^2) \qquad (2)$$

with the frequencies

$$\left.\begin{array}{ll} \nu_X^+ = \nu_Y^+ = \nu_0 \sqrt{1 + \frac{\alpha}{R^3}} & \nu_X^- = \nu_Y^- = \nu_0 \sqrt{1 - \frac{\alpha}{R^3}} \\ \nu_Z^+ = \nu_0 \sqrt{1 - 2\frac{\alpha}{R^3}} & \nu_Z^- = \nu_0 \sqrt{1 + 2\frac{\alpha}{R^3}} \end{array}\right\}. \qquad (3)$$

Here $\nu_0 = \frac{e}{\sqrt{m\alpha}}$ is the eigenfrequency of the isolated dipole. According to quantum mechanics, an oscillator with frequency   has the series of energy values $(n + 1/2)$ with $n = 0, 1, 2\ldots$ For the fixed oscillators in (2), this gives a total energy

$$E = (n_X^+ + n_Y^+ + 1)h\nu_X^+ + (n_X^- + n_Y^- + 1)h\nu_X^- + \left(n_Z^+ + \frac{1}{2}\right)h\nu_Z^+ + \left(n_Z^- + \frac{1}{2}\right)h\nu_Z^-, \qquad (4)$$

where the six numbers $\overset{+}{n_x}, \ldots \overset{-}{n_z}$ take on the integer values 0, 1, 2, 3, ... completely independently of one another. The ν_i is expanded by powers of α/R^3 and we have

$$\left.\begin{array}{l} E = h\nu_0(n_X^+ + n_Y^+ + n_Z^+ + n_X^- + n_Y^- + n_Z^- + 3) \\ \quad + \frac{h\nu_0}{2}\frac{\alpha}{R^3}(n_X^+ + n_Y^+ - 2n_Z^+ - n_X^- - n_Y^- + 2n_Z^-) \\ \quad + \frac{h\nu_0}{8}\frac{\alpha^2}{R^6}(n_X^+ + n_Y^+ + 4n_Z^+ + n_X^- + n_Y^- + 4n_Z^- + 6) + \cdots \end{array}\right\} \qquad (5)$$

The first term is independent of R; it represents the characteristic energy of the two molecules individually.

The second term (first approximation) is based on a resonance distortion caused by "energy exchange" (mirror symmetry) ([2], Chapter 2, Section 5). It definitely vanishes for the ground state ($n_x^+ = n_y^+ = \ldots n_z^- = 0$) and, since we will not concern ourselves here with the forces between excited molecules, we can disregard any further consideration of it. Dipole type force effects are involved with a potential proportional to $\pm 1/R^3$ (attraction as often as repulsion) which always appear between two systems when an energy quantum of one system "fits" into the other /226 system, i.e., when resonance is present in the quantum mechanical sense, and also if the particular transition is not subject to any forbidden selection. In practice, this case therefore appears only between similar and partly excited systems; it will perhaps play an important role in the explanation of certain photochemically produced molecular forces [3], because the forces in question can always predominate as first order effects over the molecular forces which exist between unexcited molecules.

The third term of (5) (the second approximation) is involved primarily in the interaction between unexcited molecules; attractive forces are involved under all conditions.[1] For the deepest state ($n_x^+ = n_y^+ = \dots n_z^- = 0$) we extract specially from (5) the interaction energy

$$\varepsilon = -\frac{3}{4}\frac{h\nu_0\alpha^2}{R^6}. \tag{6}$$

If we had quantized the oscillators in the sense of the earliest concept of the quantum theory "as integers" [$nh\nu$ instead of $(n+1/2)h\nu$], then we would have omitted the 3 and 6 in (5) and would have found no interaction energy whatsoever in the deepest state. This is in complete agreement with the fact that resting oscillators, according to classical theory, do not polarize one another if they do not already possess a multipole to begin with. The appearance of forces in the normal state is therefore exclusively related to the presence of a zero point motion; they are based on a mutual disturbance of this zero point motion and generally do not differ from short period disturbances, in the sense of classical theory.

Hence, the eigenfunctions of the molecular pair in the ground state can be made up directly from the known features of the harmonic oscillator, and we can see that the undisturbed function

$$\psi_0 = e^{-\frac{\pi m \nu_0}{h}(\mathfrak{r}_1^2 + \mathfrak{r}_2^2)}$$

is transformed by the disturbance into a function ψ of the following form (we use local polar coordinates and expand by α/R^3): /227

$$\psi = e^{-\frac{\pi m \nu_0}{h}(\mathfrak{r}_1^2 + \mathfrak{r}_2^2)}\left\{1 - \frac{\alpha}{R^3}\frac{2\pi m\nu_0}{h}(x_1x_2 + y_1y_2 - 2z_1z_2) + \frac{\alpha^2}{R^6}(\;) + \cdots\right\}. \tag{7}$$

The square of this function, as we know, gives each configuration of the system a certain relative probability. As we easily can see, the configurations with dipole attraction are weighted more heavily, while those with repulsion (on the other hand) are given less statistical weight, without the molecules individually receiving an average dipole moment in the process [$\overline{\mathfrak{r}_1} = 0$, $\overline{\mathfrak{r}_2} = 0$, but $(\overline{\mathfrak{r}_1\mathfrak{r}_2}) \neq 0$].

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[1] The fact that attractive forces always result in this case for the excited state is probably a special property of the harmonic oscillator. On the other hand, it can generally be shown [1, p. 251] that molecules in the normal state always attract one another in the second approximation, regardless of how the molecules are produced.

In these discussions, for lack of more empirical data, we will frequently make use of the simple Formula (6). For the case that only one excited state can be reached, beginning at the ground state (or still more generally: if all of the states that can be reached with significant transition probability from the ground state) have a small energy difference between them (small relative to the energy difference between these states and the ground state), (6) remains in effect even for this case, regardless of how the molecules in general were produced. We will show this later on.

The entire consideration is limited to distances R under all conditions, which satisfy the condition $R^3 >> \alpha$. For $R^3 < 2\alpha$, ν_z^+ becomes imaginary, i.e., the two oscillators no longer oscillate around their resting positions, but are torn apart mutually aperiodically; in addition, with respect to these distances, the spatial extent of the dipoles is in no way to be disregarded and the use of the Hamiltonian (1) is no longer legitimate.

§2. THE ADDITIVITY OF THE MOLECULAR FORCES

This remarkable property of the molecular forces will not be demonstrated on the special model of the previous section, but in complete generality for any molecule.

It has already been pointed out [1, Section 2] how the interaction energy of two molecules at a fixed distance R can be obtained approximately if the eigenfunctions of the two molecules are given.

Let one molecule be described by the series of eigenfunctions /228
ψ_0, ψ_1, ψ_2 ... with the corresponding eigenvalues E_0, E_1, E_2...; the other molecule, which is either like the first or unlike it, will be described by the eigenfunctions ϕ_0, ϕ_1, ϕ_2... and the eigenvalues F_0, F_1, F_2... . We will also have V as the function of the interaction between the two molecules, which assigns the classic potential value to every configuration of electrons and nuclei, and as such is therefore independent of the position coordinates of all components of the molecule (Coulomb potential). As we know, V has the ability to decompose into a sum whose individual summands depend on only two different particles.

This permits us to develop an approximation method in the usual manner, which shows the interaction energy ε_{kl} of a molecule in a state ψ_k with another in the state ϕ_l, both of them located at a fixed distance R from one another, and it takes the form of a series of successive approximations

$$\varepsilon_{kl} = \varepsilon_{kl}^{(1)} + \varepsilon_{kl}^{(2)} + \varepsilon_{kl}^{(3)} + \cdots$$

using the specific integral[2]

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[2] The asterisk (*) stands for the transition to complex conjugates.

$$V_{kl,\,k'l'} = \int V \psi_k \varphi_l \psi_{k'}^* \varphi_{l'}^* d\tau_1 d\tau_2, \tag{8}$$

where the integration is to be extended over all configurations of the molecular components at fixed molecular centers of gravity. These integrals (8) are functions of the distance R between the centers of gravity of the molecules, which is to be treated in integration as a constant parameter. The disturbing energy in the first approximation, i.e., the interaction of the two molecules without consideration of the fact that they deform one another mutually, is given by the expression

$$\varepsilon_{kl}^{(1)} = V_{kl,\,kl}, \tag{9}$$

the disturbing energy in the second approximation is given by the expression

$$\varepsilon_{kl}^{(2)} = \sum_{k'l'} \frac{|V_{kl,\,k'l'}|^2}{E_k + F_l - E_{k'} - F_{l'}} \quad (k', l') \neq (k, l) \tag{10}$$

etc. Hence, the method is applicable in this form only when the following condition is fulfilled:

$$|E_k + F_l - E_{k'} - F_{l'}| \gg |V_{kl,\,k'l'}|. \tag{11}$$

It is true that for a number of terms in (10), this condition is not fulfilled; we will come back to this later on, but we will initially disregard this limitation.

/229 The first order term $\varepsilon_{kl}^{(1)}$ essentially offers only forces with a short distance range; if the total angular momentum disappears, $\varepsilon_{kl}^{(1)}$ behaves asymptomatically like $R^n e^{-\beta R}$, and if the total angular momentum of the molecule is nonzero, a slight quadruple potential is superimposed, which is independent of the orientation of the rotary impulses to one another, and is based on the fact that a rotating molecule has quadrupole symmetry in average time.[3] For large distances, as we can easily demonstrate, these effects are proportional to[4]

$$\frac{1}{R^5} \{J(J+1) - 3m^2\} \{J'(J'+1) - 3m'^2\} \tag{12}$$

(J, J' = the total angular momenta of the two molecules, m, m' = projection of the latter on the line connecting the centers of gravity of the molecules). On the average, they disappear for all orientations of the molecules and in general do not appear to be of very great interest from the physical point of view. In atoms, these effects occur as manifestations of the so-called l-valences [4]; with regard to the latter, we do not know at the present time to what extent a principal significance for chemistry can be assigned to them.

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[3] This is a correction of an erroneous statement in [1, p. 248].

[4] For $|m| = |n| = 1$, we have an additional term $\pm \dfrac{J(J+1)J'(J'+1)}{8R^5}$.

The case of the "molecules", in contrast to that of the "radical", is distinguished primarily by the fact that in the first approximation, i.e., as long as the internal structure of the specific system does not undergo disturbance, no noteworthy attractive forces appear. The first approximation effects then essentially characterize the cross section of the molecules and their compressibility; both are data based on such short distances in the molecules that their wave-mechanical calculation would require a quite detailed knowledge of the molecular periphery.[5] However, we do not know the eigenfunctions of the molecules exactly, so we will omit these data from consideration since they are relatively easy to measure. This procedure is even more to be recommended, since the first approximation alone would offer a very inexact figure for these distances even if one could calculate it.

The effects which appear in the second order, on the other /230 hand, are of much greater distance range [2]; hence they can be determined even with a relatively summary knowledge of the molecular structure. They even give a rather good idea of the attraction possibility of the molecules, since the other effects are of short distance range and are introduced very suddenly at short distances. To this extent, it is also justified to consider these forces separately and to determine them theoretically while leaving the others out of consideration.

We will now discuss at the same time still a third molecule with the eigenfunctions χ_0, χ_1, $\chi_2 \ldots$ and eigenvalues G_0, G_1, $G_2 \ldots$ and at a fixed distance S from ϕ and T from ψ. Then the total interaction energy of the second order of the three molecules in the states ψ_k, ϕ_l, χ_m will be

$\psi_k, \varphi_l, \chi_m.$

$$\varepsilon^{(2)}_{klm} = \sum_{k'l'm'} \frac{|W_{klm,\,k'l'm'}|^2}{E_k + F_l + G_m - E_{k'} - F_{l'} - G_{m'}} \qquad (k'l'm') \neq (klm) \tag{13}$$

with

$$W_{klm,\,k'l'm'} = \int W \psi_k \varphi_l \chi_m \psi^*_{k'} \varphi^*_{l'} \chi^*_{m'} \, d\tau_1 \, d\tau_2 \, d\tau_3. \tag{14}$$

Here, W decomposes into three components as a Coulomb potential function, each of which depends only on the particles of two molecules and their distances:

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[5] The conditions in this respect are more favorable for the radii of ions. See [5].

$$W = \sum_{\alpha\beta} \frac{e_\alpha e_\beta}{r_{\alpha\beta}} + \sum_{\beta\gamma} \frac{e_\beta e_\gamma}{r_{\beta\gamma}} + \sum_{\gamma\alpha} \frac{e_\gamma e_\alpha}{r_{\gamma\alpha}}. \tag{15}$$

(e_α = charges of the particles of the first molecule, e_β of the second molecule, e_γ of the third molecule, and $r_{\alpha\beta}$, $r_{\beta\gamma}$, $r_{\gamma\alpha}$ = the corresponding intermolecular distances). Hence, all terms of $W_{klm,\ k'l'm'}$ with $k \neq k'$, $l \neq l'$, $m \neq m'$ disappear owing to the orthogonality of the eigenfunctions. There remain only those terms in which either $k = k'$ or $l = l'$ or $m = m'$. It will then be advantageous, instead of $W_{klm,\ k'l'm'}$, to introduce the three functions $V^{\psi\phi}_{(R)}$, $V^{\phi\chi}_{(S)}$, $V^{\chi\psi}_{(S)}$:

$$\left.\begin{aligned} W_{klm,\,k'l'm} &= V^{\psi\varphi}_{kl,\,k'l'} \quad (R) \\ W_{klm,\,kl'm'} &= V^{\varphi\chi}_{lm,\,l'm'} \quad (S) \\ W_{klm,\,k'lm'} &= V^{\chi\psi}_{km,\,k'm'} (T) \end{aligned}\right\} \tag{16}$$

since all other terms disappear. Then we see immediately that the triple sum (13) breaks up into three double sums, each of which depends on only two of the three molecules and their distances:

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$$\left.\begin{aligned} \varepsilon^{(2)}_{klm}(R, S, T) = &\sum_{k'l'} \frac{\left|V^{\psi\varphi}_{kl,\,k'l'} \ (R)\right|^2}{E_k + F_l - E_{k'} - F_{l'}} \\ &+ \sum_{l'm'} \frac{\left|V^{\varphi\chi}_{lm,\,l'm'} \ (S)\right|^2}{F_l + G_m - F_{l'} - G_{m'}} \\ &+ \sum_{m'k'} \frac{\left|V^{\chi\psi}_{mk,\,m'k'} (T)\right|^2}{G_m + E_k - G_{m'} - E_{k'}} \end{aligned}\right\} \tag{17}$$

The first component on the right-hand side corresponds throughout to the expression given in (10) for the interaction of the two isolated molecules ψ_k and ϕ_l. It depends only on the distance R, and on this distance alone. When the third molecule is added, the potentials which depend only on the distance of the third molecule from the first two overlap additively, i.e., the force which counteracts the change of the distance between the first two molecules (the differential quotient of the total potential for this distance) is not affected by the presence of the third molecule.

The result here seems to be a quite trivial result of the additivity of the Coulomb potential functions. But it is by no means so self-evident, as we can see, that this additivity is not at all generally valid for forces of short distance range [6, p. 104], although there the same Coulomb potential function serves as the origin. Rather, there is a quite complex overlapping mechanism which expresses the saturation of the chemical binding forces; it is an actual fact that between two atoms there are quite different force expressions in effect, depending on whether a chemical force process has already been in effect between one of them and a third atom, or not. It is precisely in this respect that the molecular forces differ quite characteristically from the homopolar valence forces. For the first approximation, we can show that it is only in exceptional cases that the forces between two atomic systems cannot be influenced by the presence of a third, and then only when no free valences are involved. We see that in this case the rule is also valid for the forces of higher distance range of the second approximation. In the third approximation, however, there is no longer any additivity under any circumstances.

The entire concept is therefore based on the fact that condi- /232
tion (11) is fulfilled for all terms in (10). It can be broken down as follows: in the first place, while the left side vanishes exactly, i.e., if the molecular state in question is distorted. This means that we must consider primarily the following possibilities:

(a) Directional distortion of the orbital angular momentum,
(b) Directional distortion of electron spin,
(c) With similar molecules, distortion caused by energy exchange (mirror symmetry).

We have already discussed case (a) at the beginning of this section (12). The additions which it causes appear to be insignificant, but nothing conclusive can yet be stated with regard to them.

Case (b) gives rise to effects which are not additive, the valence type effects which were mentioned above. However, since the latter are of short distance range, we can simply put primes on those particular terms for large molecular distances. [This has been down from the start in (10) and (8)]. Aside from this, in general we will have the case that the resultant electron spin of the molecules is zero, so that there is no distortion in this respect and there is additivity even for short molecular distances.

Case (c) represents a considerable limitation of our consideration. It is always found when one system can adopt an energy quantum from the other and if no forbidden selection has been imposed on the specific transitions; it offers a nonadditive effect in the first order which is of much greater distance range than the forces which we have discussed thus far. We have already encountered these forces in special form in the discussion of the second term of (5). However, as long as we do not have to deal with excited molecules, these effects do not appear; they differ basically from the usual molecular forces.

In the second place, condition (11) can be eliminated if the left side is nonzero but small. Since $V_{kl,\ k'l'}$ are dependent upon

R and vanish with increasing R in this case the condition is eliminated only for molecular distances below a certain limit; for larger distances, the considerations regarding additivity are retained in any case. This case shows up practically only in the case of the densely packed rotation level of the molecule and is based /233 (generally speaking) on the conversion of the rotational movement of the free or far-apart molecules into a cycling around the equilibrium sites when the latter are brought sufficiently close together. Effects of first approximation also appear at this time, which are not additive in any sense of the word any more than the static mutual interactions of molecules superposed upon one another according to the classic theory, which are in complete correspondence to them.[6]

If we expand V in powers of $1/R$ then we obtain (if both molecules are neutral, as we assume) a series which begins only with the third term with which we break off:

$$V = \frac{e^2}{R^3}[\xi_1\xi_2 + \eta_1\eta_2 - 2\zeta_1\zeta_2] + \cdots \tag{18}$$

Here $e\xi_1$, $e\eta_1$, $e\zeta_1$ stand for the components of the electrical moment of one given configuration of all the components of a molecule while $e\xi_2$, $e\eta_2$, $e\zeta_2$ are those of the other. Accordingly, for $V_{kl,\ k'l'}$ we obtain the series whose first term is also proportional to $1/R^3$ and which generally, on the basis of the relationship

$$\left|\int \xi \psi_k \psi_{k'} d\tau\right|^2 + \left|\int \eta \psi_k \psi_{k'} d\tau\right|^2 + \left|\int \zeta \psi_k \psi_{k'} d\tau\right|^2 = \frac{f_{kk'}}{E_{k'} - E_k}\frac{3h^2}{8\pi^2 m}$$

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[6] The transition from rotation into liberation has already been discussed in this paper (§ 9) for dipoles on the basis of a very simple perturbation theory treatment. However, I would like to point out that the latter is applicable in sufficient approximation only for the ground state of this transformation and the method of approximation must be continued further for the excited state. For a quite rough consideration, the classical viewpoint will suffice, which involves the magnetude of the kinetic energy of the rotational movement; depending on whether the latter is larger or smaller than the maximum value of the potential energy of the molecules taken together, the motion will show a rotatory or oscillatory character. In addition, we must also take into account the zero point motion, which has already been mentioned in Formulas (37) in this paper. In the case of molecules with a low inertial moment, this contribution is already on the order of magnitude of the intermolecular orientation forces and as we can easily estimate (e.g., in HI and perhaps also in HBr) it may even be sufficient to make it impossible for the molecules in the lattice bond to assume an arrangement in the preferred directions, even at the absolute zero point. See also the paper by Pauling [6]; however, I do not wish to trace in detail the statements given there.

can be represented by the dispersion f-values of the corresponding transitions.[7] We introduce this into (10), and obtain

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$$\varepsilon^{(2)}_{kl} = -\frac{1}{R^6}\cdot\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^4 \sum_{k'l'} \frac{f_{kk'}g_{ll'}}{(E_{k'}-E_k)(F_{l'}-F_l)(E_{k'}+F_{l'}-E_k-F_l)} + \text{terms of higher order.} \qquad (19)$$

Here $f_{kk'}$ and $g_{ll'}$ are the "dispersion electron numbers" which are related to the eigenfrequencies $\frac{1}{h}(E_{k'}-E_k)$ and $\frac{1}{h}(F_{l'}-F_l)$ of the molecules, and which bear the following relationship to the polarizabilities $\alpha_k(\nu)$ and $\beta_l(\nu)$ of the latter for the frequency ν:

$$\begin{aligned} \alpha_k(\nu) &= \frac{1}{m}\left(\frac{eh}{2\pi}\right)^2 \sum_{k'} \frac{f_{kk'}}{(E_{k'}-E_k)^2 - h^2\nu^2} \\ \beta_l(\nu) &= \frac{1}{m}\left(\frac{eh}{2\pi}\right)^2 \sum_{l'} \frac{g_{ll'}}{(F_{l'}-F_l)^2 - h^2\nu^2}. \end{aligned} \qquad (20)$$

Expression (20) can be used directly for determining (19). If one of the f-values is seen to be particularly higher than the rest of them, or (as is usually the case at the same time) if the energy differences which are involved ($E_{k'}-E_k$ and $F_{l'}-F_l$) are very close to one another, it will be possible to obtain a suitable average value of ΔE_k or ΔF_l for the sums in (19) and (20) and then introduce the polarizabilities, $\alpha_k = \alpha_k(0)$ and $\beta_l = \beta_l(0)$ of the two molecules for long waves, into (19):

$$\varepsilon^{(2)}_{kl} = -\frac{1}{R^6}\,\frac{3}{2}\,\frac{\Delta E_k \Delta F_l}{\Delta E_k + \Delta F_l}\cdot\alpha_k\beta_l. \qquad (21)$$

For uniform molecules ($\Delta E_k = \Delta F_l = h\nu_0$, $\alpha_k = \beta_l$) expression (21) naturally becomes the expression which was obtained earlier especially for quasi-elastic molecules (6).

With respect to the manner of writing the dispersion Formulas (20) it should be mentioned that they do not quite agree with the conventional ones if infrared eigenoscillations are present. In the latter case, it is conventional to take into account the fact that the inert nuclear masses are much easier to bring into resonance than the electrons, and therefore to extract the corresponding large masses of the atomic nuclei before the partial sums which the infrared dispersion contains in order to obtain for the latter an f-sum of the order of magnitude 1. This definition has not /235 been very apt thus far because the atomic masses involved cannot be assigned individual eigenoscillations in molecules which have more than two atoms. It would be much better even in (19) and (20) not to introduce the masses at all, for the presence of them in the dispersion formula has a completely historical foundation. The fundamental molecular properties which are involved in (19) and (20) are the Fourier components of the electrical dipole moment of the molecule, which change rapidly with time and whose terms can be obtained individually from the dispersion formula of the molecule and used directly for constructing the molecular forces.

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[7] If the resultant angular momentum of the molecule is $\neq 0$, we must introduce the f-values of the corresponding individual Zeeman components. The forces will then show a directional dependence. The variation around the average value is such because there is a quadratic effect which is very slight and is not particularly dependent on the sign of the forces. In most cases, then, it will be permissible to operate with the average value of the forces which have been averaged over all the orientations. I would like to point out once again that the forces are not to be viewed essentially as the central forces.

In this respect we have avoided writing this "mass free" representation of the formulas and have contented ourselves with extracting always one and the same mass, that of the electron. This is because the contributions of the infrared dispersion terms in most cases can be disregarded anyway and because dispersion measurements are now usually written in this form.

§3. MOLECULAR FORCES IN COMPOUNDS

It is of considerable interest to compare the attraction constants C_{ab} of forces between molecules of two different molecular types a and b with the attraction constants C_{aa} and C_{bb} which describe the forces between molecules within the individual types and . In most of the force laws known to us, such as the Coulomb or gravitation law,

$$C_{aa}C_{bb}=C^2_{ab}.$$

Expression (21) shows, however, that in the molecular forces under consideration here, owing to the identical nonequivalency

$$\left(\frac{\Delta E+\Delta F}{2}\right)^2\geqq \Delta E\Delta F$$

we must always have

$$C_{aa}C_{bb}\geqq C^2_{ab} \tag{22}$$

and that the inequality is particularly involved only for $\Delta E = \Delta F$ and this result is still valid beyond the special assumptions which are the basis of the approximation Formula (21), quite generally. For postive ν_k and μ_l we have the identical inequality

$$\sum_{kk'}\frac{f_k f_{k'}}{\nu_k+\nu_{k'}}\cdot\sum_{ll'}\frac{g_l g_{l'}}{\mu_l+\mu_{l'}}\geqq\left(\sum_{kl}\frac{f_k g_l}{\nu_k+\mu_l}\right)^2. \tag{22a}$$

The forces in a compound are therefore in general weaker than the geometrical mean of the forces in the pure substances and they are weaker by a degree which increases the further the characteristic spectral ranges of the two types of molecules are apart. /236

This effect can be considered as being definite only in the rarest cases. Usually we are missing either the value of the interaction energy for the minimal distance of the molecules or the integral of the mutual interaction of this minimum distance to infinity. In any case these are expressions which can be given in the following form:

$$A_{ab}=\frac{C_{ab}}{\left(\frac{d_a+d_b}{2}\right)^n},\qquad A_{aa}=\frac{C_{aa}}{d_a^n},\qquad A_{bb}=\frac{C_{bb}}{d_b^n},$$

where d_a and d_b are the diameters of the corresponding molecules. However, if $d_a \neq d_b$, then $\left(\frac{d_a+d_b}{2}\right)^{2n} > d_a^n d_b^n$ and

$$A_{ab}^2 < A_{aa}A_{bb},$$

even if $C_{ab}^2 = C_{aa}C_{bb}$. Such a confirmation of the compound formula could therefore be valuable in a consideration of this circumstance; merely from the distortion of compound diagrams we generally cannot draw any firm conclusions. In the opposite case, however, when the effects of the compound forces exceed the geometrical means, we can say with confidence that forces of some other type must be involved, such as specifically effective valence forces, etc.

§4. LATTICE ENERGY OF MOLECULAR LATTICES

Of those applications which molecular forces can find, we should stress especially those which are based on the relationships determined empirically long ago between the van der Waals attraction effects and the surface forces as well as the heats of sublimation of molecular lattices, and which could not be explained at all satisfactorily with the idealized concepts previously employed. For example, in the series of hydrogen halides HCl, HBr, HI the heats of sublimation S increase while the dipole moments μ of the molecules and their reciprocal distances $1/R$ decrease in the solid state; it is therefore of no advantage to attribute the lattice energy of the solid hydrogen halides to dipole effects alone (see [8] and [9], its review in the Handbook of Physics, Vol. 24, the article /237
by Born and Bollnow on p. 450). In any case the polarizability α increases in a series. However, the possibility of producing an induced dipole moment by polarization is not involved for reasons of symmetry in the solid state; in any case, it would involve the product $\alpha\mu^2$ which decreases sharply in the series under consideration.

TABLE 1. /237

	$\mu \cdot 10^{18}$	$\alpha \cdot 10^{24}$	$R \cdot 10^{8}$	S in Kcal/Mol
HCl	1·03	2·63	3·89	5·05
HBr	0·78	3·58	4·17	5·52
HI	0·38	5·39	4·5	6·21

The short-period interactions with which we are concerned, on the other hand, are not subject to the latter objections; they superpose themselves additively in the lattice bond in the first approximation and since they behave in proportion to α^2 and are independent of the inertia μ there is a possibility for attributing the increase in lattice energy mainly to them.

Naturally the dipole moments will also make a certain contribution to the lattice energy, but we can estimate that the latter must be very small in this case.[8] We will therefore begin by calculating the lattice energy of these lattices without considering the slow periodic terms which contain the dipole effects and other forces which depend on the orientation. The potential between two molecules which are at rest at a mutual distance R is written as follows:

$$\varphi = -\frac{C}{R^6} + b(R). \qquad (23)$$

The attraction potential $-\frac{C}{R^6}$ can be given by Equation (6) and possibly by (19), while the repulsion $b(R)$ which appears primarily in the first approximation of the defect process, cannot be given; we know that it vanishes somewhat like $R^n e^{-\beta R}$, in other words rather suddenly, where n is approximately equal to 3 [11]. Therefore, /238 it does not appear very suitable to use here the conventional exponential equation for the repulsive force, because the repulsive force breaks off more suddenly than any power. The experimental data from which we are accustomed to calculating the repulsion law, compressibility and thermal expansion, more accurately provide only the second and third derivations of the potential at the equilibrium configuration; however, for the consideration of the absolute value of the potential, the precise form of the repulsion potential is critical and it is completely anticipated by the exponential equation. We can attempt to determine the constants in the above-given $b(R)$ from experimental data, but in view of the inaccuracy of the balance of the calculation, I did not consider it worthwhile to go into such detail precisely on this point. For a first orientation, we will assume that the power $\phi = -\frac{C}{R^6}$ extends from infinite distances up to the equilibrium configuration and it can then suddenly make a sudden jump to + ∞ for smaller distances. We will obtain the distance in the equilibrium position from the measured lattice constants. The model is naturally not suited for showing the compressibility, but it will suffice to illustrate the energy relationships in analyzing the lattice; in general, there is nothing against refining the model at any time in the sense indicated.

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[8] See [1], pp. 277-278. It has already been pointed out in [10] that in the HCl lattice of the modification which is stable above 98°, the molecules are free to rotate. A rather crude estimate of the dipole forces in the lattice shows that the directional forces of the temperature movement no longer exist at this temperature. In the case of HI, the directional forces are so weak that they can be overcome by the zero point movement alone.

As the lattice energy at the absolute zero point, we then have

$$\Phi = -\frac{C}{2} N_L \sum_i \frac{1}{R_i^6} = -\frac{C}{2} \frac{N_L}{d^6} \sum, \qquad (24)$$

where

$$\sum = \sum_i \left(\frac{d}{R_i}\right)^6 \qquad (25)$$

N_L is Loschmidt's number, R_i is the distance of a central atom which is fixed in the summation, i.e., located far beneath the surface, from another atom in the lattice marked with i; the sum is taken over the entire lattice and converges very rapidly. d represents the lattice constant.

The sum $\sum_i \left(\frac{d}{R_i}\right)^6$ was calculated for the face-centered cubic lattice, since the latter is the one most often encountered. Up to $R = 3d$, direct summation over the 458 molecules involved gives a value of 117.42. For the rest from $R = 3d$ up to infinity, we find, by integration, the contribution $\frac{16\pi}{81} = 0.62$. In general, we obtain a rather exact value of 118.0 for Σ with an error of less than 1%. The lattice energy of the face-centered lattice is therefore /239

$$\Phi = -\frac{59 C N_L}{d^6}. \qquad (26)$$

For calculating C, for lack of better data, we will generally use Equation (6). In some of the materials under consideration, rather precise dispersion formulas are already known. They indicate that very often a single frequency makes such an overwhelming contribution both to the molar refraction as well as to the molecular forces that the other terms of the dispersion formula can be disregarded. In saturated molecules, this principal frequency ν_0 appears to lie mostly in the immediate vicinity of the series boundary, and even shortly behind it in the continuum [12]. To the extent that it was possible, we employed these data and were able to use the simple Formula (6) for calculating C since we were dealing with single-term dispersion formulas throughout. Values not very different from these are obtained if we use as the principal frequency ν_0 the series boundary; this makes it possible for us to obtain a certain degree of justification for our method since in a few cases, for lack of better data, we relied only on the series boundary since the electron configuration of the molecules involved is not very different from that of the others (rare gas shell in HCl, etc). The figures which use only the series boundary are given in the following in parentheses. If we express $h\nu_0$ in calories per mole from ($J = N_L h\nu_0$), then we also obtain Φ in calories per mole:

$$\Phi = -\frac{3}{4} \cdot \frac{59\,\alpha^2 J}{d^6} = -44{\cdot}25\,\frac{\alpha^2 J}{d^6}.$$

It is often more suitable to carry out the calculation using the density ρ instead of the lattice constants. For the face-centered cubic lattice, we have

$$\varrho = \frac{4M}{d^3 N_L}.$$

(M = molecular weight). Then for the lattice energy, we have

$$\Phi = -\frac{3}{64}\,59\left(\frac{N_L \varrho}{M}\right)^2 \alpha^2 J = -1{\cdot}015 \cdot 10^{48}\left(\frac{\varrho\,\alpha}{M}\right)^2 \cdot J. \qquad (27)$$

Table 2 lists the heats of sublimation ($S = -\Phi$) of the hydrogen halides calculated according to this formula and a few other molecular lattices and they are compared with the empirical values.[9] The formula, strictly speaking, is applicable only at the absolute zero point, since it contains only a contribution of the potential energy. It must therefore be compared with the heats of sublimation extrapolated to the absolute point, and the extrapolation will be carried out in the classical manner since we also have disregarded, in theory, the zero point motion. In the case of argon and in the modification which is stable below 98° for HCl the structure is found to be actually cubic face-centered [10], as for N_2 and CO [12a]. X-ray analytical structural measurements are lacking for the other materials; for the large part, they all show different modifications, but the $\sum \left(\frac{d}{R_i}\right)^6$ in general may show a contribution /240 per mole which is not very different from that of the closest packed structure. In general there is not the slightest difficulty in also

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[9] In the discussion of the empirical material, I had the kind assistance of Prof. Simon, as well as Miss Zarniko; I would like to thank both of them at this point.

TABLE 2. THEORETICAL AND EMPIRICAL HEATS OF SUBLIMATION

	ρ (0° abs.)	$\alpha \cdot 10^{24}$	M	J in kcal/Mol	theoretical heats of sublimation in kcal/mol	meas. heats of sublimation extrapolated to 0°	remarks
Ne	1·46	0·39	20·2	(491) 592	(0·40) 0·47	0·59	
N_2	1·03	1·74	28·02	(391) 396	(1·61) 1·64	1·86	
O_2	1·43	1·57	32·00	(299) 339	(1·48) 1·69	1·89 2·06	upper modification lower ”
A	1·70	1·63	39·88	(354) 402	(1·83) 2·08	2·03	
CO	1·05[10]	1·99	28·00	(329)	(1·86)	2·09	$\mu = 0{\cdot}12 \cdot 10^{-18}$
CH_4	0·53[14]	2·58	16·03	(334) 326	(2·47) 2·42	2·70	
NO	1·58	1·76	30·01	(235) 332	(2·04) 2·89	4·29	polymerization
HCl	1·56	2·63	36·47	(315)	(4·04)	5·05	$\mu = 1{\cdot}03 \cdot 10^{-18}$
HBr	2·73	3·58	80·93	(306)	(4·53)	5·52	$\mu = 0{\cdot}78 \cdot 10^{-18}$
HJ	3·51	5·40	127·93	(292)	(6·50)	6·21	$\mu = 0{\cdot}38 \cdot 10^{-18}$
Cl_2	2·0	4·60	70·92	(419)	(7·18)	7·43	

evaluating the corresponding very rapidly converging lattice sums in case we are also interested in other types of lattices. The densities are extrapolated to the absolute zero point as though /241 the substances had no critical point. In general, the difference caused by the different modifications is very small (except in the case of O_2).

Naturally the data contained in the table are to be considered only as a first crude approximation, but we can see that the forces which we have placed in the foreground are critical for the order of magnitude of the lattice energy of this molecular lattice and that they especially give the pattern of the latter within the entire series correctly without exception; thus, e.g., the HI-lattice is held together by basically the same forces as the argon lattice. At the points which show greater deviations, we can also expect theoretical deviations downward, since here other forces are to be taken into consideration: in HCl and HBr the dipoles are not completely ineffective for the pattern of the heats of sublimation primarily, as according to previous theories. In NO, there is a strong tendency toward polarization in the liquid state, which is also expressed, e.g., in an abnormally large value for the Trouton constant of NO. In general, all of the theoretical values seem to be too small; this is particularly startling when we realize that the forces of repulsion which we have disregarded would make the theoretical values still smaller. On the other hand, however, in crystallized N_2, CO, etc., in which fixed orientations of the molecules have been determined by x-ray analysis, the directional forces cannot be completely disregarded so that at such short distances it is no longer possible, strictly speaking, to idealize the molecules simply as fixed force centers, i.e., to disregard the higher approximations.

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[10] See [12a]. The measurements are based on approximately 20° absolute temperature. The molecules are rotationless in the corresponding modification.

An effective control over all these additional conditions can scarcely be expected. Therefore, we will have to place stricter demands on the accuracy of the numerical determinations. However, our own consideration appears to indicate that if we wish some general idea of the force effects which are developed and are acting here, we must think primarily of the attraction forces which are particularly simple here. Naturally, the bigger and more complex a molecule becomes, the greater become the orientation forces which are produced by the pure space problem of the orientation. In these molecules, we will not be able to get any idea of the force effects /242 without considering other details. This circumstance makes itself particularly clear even in the relatively elongated CO_2-molecule.

If we compare expression (26) for the heats of sublimation with that given in (16) for the van der Waals a, or with the critical temperature T_k taken from this a together with the van der Waals b, we get:

$$\frac{\Phi}{T_k} = \text{const},$$

which is the familiar Pictet-Trouton rule. In any case, the determination of the constants on the right side is blocked by the uncertainty that the van der Waals b is characterized by that molecular distance at which the interaction potential disappears, while for the lattice energy the somewhat greater distance of the potential minimum is critical. If we assume the latter distance to be about 21-24% greater than the former [15], then we get the empirical value 13-15. In this respect, we should note that Φ does not stand for the heats of evaporation but rather for the heats of sublimation at absolute zero; the point T_k represents the critical and not the boiling point. Since the value of the theoretical constant also varies very strongly with the fixed power of the assumed distance, no particular importance can be attributed to the numerical determination of the Trouton number.

§5. APPLICATION TO GAS ADSORPTION[11]

The idea has frequently been expressed that the surface forces which are effective in the phenomena of adsorption could be identical with the van der Waals forces [16, 17]. According to what was said at the beginning, it is understandable that as long as we limit ourselves to electrostatic effects [18, 19] this relationship does not receive any satisfactory theoretical explanation since in the case of an overlapping of electrostatic forces of the in- /243 dividual molecules of an adsorbing wall, a considerable compensation of the effects outward is unavoidable. If, however, as E. Hückel pointed out in his book [20, N.B. p. 126] , apparently correct orders of magnitude are obtained for the electrostatic interpretation of the adsorption forces and for different models of the wall and adsorbate, he was able to do this only if he acted on the basis of the distance of the adsorbate from the wall atoms, which is less than the distance between the atoms inside the walls; consequently, he is satisfied by the fact that (extrapolated to such small distances) quadrupole forces can provide greater contributions than dipole forces. This is a criterion for the fact that the range of competence of the dipole and quadrupole theory has already been exceeded.

In many cases, it is undoubtedly true that charges, dipoles, and free homopolar valences will make themselves considerably prominent on the wall surfaces. The effects, for which characteristically even the sign of the forces changes from place to place over stretches on the molecular scale, and which therefore underlie the mobility of the adsorbate along the wall to a considerable extent, should really be considered as more than chemical polar or homopolar bonds. The typical case of adsorption seems to be particularly marked by the fact that the adsorbate (even in the film) shows a considerable mobility along the wall[12] and should be considered there as a van der Waals gas.

I am presenting here a compendium [22] of those signs which would be viewed as significant from the phenomenological viewpoint for the ideal case of pure adsorption. It is understandable that an idealization of this type for the conditions always avoids only an approximation in reality:

1. The adsorption forces are independent of temperature.

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[11] See in this respect an article by M. Polanyi and the author regarding this subject which is being prepared for publication in the journal Naturwissenschaften.

[12] See the experiment by Volmer and Adhikari [21].

2. The adsorption force, which acts on an adsorbed molecule at a given point, is independent of whether the neighboring region is filled by adsorbed molecules of some type or not.

3. The adsorption forces do not influence the internal forces which act between the adsorbed molecules; therefore, the same state equation which applies to the adsorbed material in the usual state /244 is also applicable to the adsorbed layer.

For this concept (developed primarily in [23, 24, 25, 26]) which was not directly justifiable from the viewpoint of the electrostatic theory and therefore has been repeatedly attacked, the molecular forces mentioned here give the desired explanation. Even if these forces, corresponding to the lattice structure of the adsorbent, will not be exactly constant along the wall, they will still vary within relatively narrow limits and in any case will not change their sign locally. Moreover, this makes it possible to consider the adsorbed gas (even inside the film) still as a gas and to assign to it a certain mobility and free path length. In addition, according to the previously proven superposition principle of the molecular forces, we can assume that the forces which prevail between two adsorbed molecules will be modified relatively slightly by the adsorbent so that in the first approximation, we can operate even in the adsorbed layer with the van der Waals forces of the free gas. Finally, our molecular forces contain at least one important component which is independent of temperature, since its average value does not disappear completely over all orientations. In general, the forces are almost completely independent of the orientation of the molecule and therefore of temperature as well.

Given the attraction potential ϕ of an atom or molecule of the adsorbent designated by i, calculated on the basis of (21) with a molecule of the adsorbate at a distance R_i

$$\phi = - \frac{C}{R_i^6} .$$

From this we can calculate the potential of the molecule relative to an entire wall at a distance d with particular simplicity, if we keep in mind that generally the distances of the wall atoms from one another can be smaller than the distance at which the adsorbed molecules can approach the wall atoms so that the summation over the atoms of the wall can be replaced by an integration. At these distances the forces no longer show any considerable variations which reflect the lattice structure of the wall. Thus for an infi- /245 nitely long wall, we obtain as the adsorption potential:

$$\Phi_{\text{ads}} = \iiint \frac{C}{R^6} \cdot N\,dv = \frac{N\pi C}{6} \cdot \frac{1}{d^3} . \qquad (28)$$

Here N is the number of atoms of the wall per cubic centimeter.

The exponent of the potential is naturally reduced by 3 in integration over the three dimensions of the wall so that the effect is proportional to the density of atoms of the adsorbent. According to its derivation, the formula is, of course, only applicable for $d > \frac{1}{\sqrt[3]{N}}$, which usually is the case. The forces decrease relatively slowly with distance from the wall, much more slowly than the forces of the electrostatic models usually discussed. If we use the special value of (21) for C, then we obtain as the adsorption potential:

$$\Phi_{\text{ads}} = \frac{N\pi}{4} \frac{\alpha\alpha'}{d^3} \frac{JJ'}{J+J'}. \tag{29}$$

Here the values with primes on them can be used for the adsorbents.

It is scarcely possible at the present time to evaluate (29) because the required experimental data are lacking. In particular, we lack knowledge of the characteristic energies J' for the adsorbents. It may be that the infrared eigenoscillations may often play a significant role here so that we could use the more precise Formula (19). Many of the adsorbents are conductors; in this case the picture which we have developed here is completely wrong, although it would not be difficult to make a similar study of the short-period defects of the electron movements in a metal.

In order to have at least some idea of the size ratios, let us calculate the following model which may have more than fictional value: as the polarizibility α' of the adsorbent, let us take a value which is obtained from the atomic refraction of carbon, $\alpha' = 0.87 \cdot 10^{-24}$, as the density, that of graphite (2.23), i.e., $N = 0.113 \cdot 10^{24}$. For J' let us select the value of 259 kcal, which corresponds to the ionization voltage 11.2 volts of C [27]. Then we get for the adsorption potential of a gas with polarizability α and characteristic energy J at a distance d:

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$$\Phi_{\text{ads}} = \frac{0.113\,\pi}{4} 0.87 \cdot 259 \cdot \frac{J\alpha}{d^3(259+J)} \text{ kcal pro Mol}$$
$$= 200 \frac{J\alpha}{d^3(259+J)} \text{ kcal pro Mol.}$$

The minimum distance d is divided into

$$d = \frac{d_1}{2} + \frac{d_2}{2},$$

where $\frac{d_1}{2} = 1.67$ Å stands for the half-distance of the layers of the graphite lattice. We will assume that for molecules which do not react chemically with carbon atoms, the critical atomic radius of carbon is that which regulates the relatively large distances between these related layers that are evidently not connected by chemical valences. It may that the forces which the layers of a layer lattice exert on one another are identical to those discussed here; in any case this calls for further corroboration. d_2 is the molecular radius of the adsorbed gas, taken from van der Waals b. If we go on to calculate over 40% of the repulsive force (naturally, quite arbitrarily), which would correspond to a repulsion exponent $n = 10.5$, we obtain:

TABLE 3. HEATS OF ADSORPTION

	$\alpha \cdot 10^{24}$	$d^3 \cdot 10^{24}$	J in kcal/Mol	Φ_{ads} (theor.) in kcal/Mol	Φ_{ads} (exper.) in kcal/Mol
He	0·20	27	589	0·62	0·615
N_2	1·74	34·3	396	3·7	3·23
A	1·63	30·9	402	3·8	3·59
CO	1·99	33·4	(329)	(4·0)	4·08
CH_4	2·58	35·6	326	4·9	4·87
CO_2	2·65	38·8	394	5·0	5·56

We selected all those substances which were collected by Hückel [20] as well as data for the theoretical treatment. The agreement of the theoretical and experimental figures is so considerable that we feel it necessary to warn against drawing too many conclusions from them. The simplifications used as a basis are very considerable if we have made a calculation which is at least provisory for the influence of the repulsive forces so that the agreement of the data as far as order of magnitude is concerned should really be taken as a confirmation. In particular, the experimental data themselves are very difficult to interpret: the value of the adsorp- /247
tion energy is dependent on the concentration of the adsorbed gas and it is not easy to decide whether at smaller concentrations one would not be getting too high values, while the gas is first caught in splits and cracks in the wall, in which naturally there would be a higher potential than on a flat surface. On the other hand, at high concentrations, the adsorption potential due to mutual trapping of the gas molecules is generally reduced. In addition, we would also have to discuss the adsorption energy at the absolute zero point for comparison. However, there does not appear to be the slightest degree of inaccuracy in the fact that all the measurements refer to charcoal and not to graphite. All of this must remain undiscussed here. The fact that the theoretical values agree so precisely nevertheless should be viewed as purely accidental.

In view of the extraordinary complexity of the situation, the lesson of the theory does not seem so much to be that of offering numerically precise data which can be matched against experimental data only very inaccurately, but rather of presenting a proof that the theories already existing, which are mainly phenomenologically oriented and which appear to largely contradict the balance of our knowledge of atomic physics, actually appear to be justified to a considerable extent today.

Similarly to the Pictet-Trouton rule, we can also derive a corresponding relationship:

$$\frac{\Phi_{\text{ads}}}{\sqrt{T_k}} = \text{const}$$

at least if we assume for the sake of simplicity that the value of Φ_{ads} has already been determined to a considerable extent by its dependence upon α (cf. Table 3); this means that we can disregard the deviations from the mixing relationship discussed in § 3. We will avoid going into other details here as far as this relationship is concerned; Eucken has already pointed out the relationship between the van der Waals and adsorption forces so that we have nothing particularly new to add to it. Aside from this, however, we would like to assign a quite heuristic significance to this relationship to an increased extent, since as we have said it can be derived only on the basis of a disregard of factors which are not always insignificant.

§6. MOLECULES WHICH ARE BOUND BY VAN DER WAALS FORCES /248

Recently, band systems have been investigated whose carriers are extremely loosely bound molecules and which one usually thinks of as being held together by van der Waals forces, since we usually think of compounds with chemically inert materials such as rare gases. We are in a position to offer a quantitative basis for this interpretation by calculating the dissociation energies of those molecules. These are the molecules Hg_2, HgKr, HgA.

For Hg we have a detailed dispersion formula [28] so that when we can use the more precise Formula (19) which is extremely valuable to us since the Hg-spectrum (owing to its considerable length) does not permit use of the simple Formula (6) any longer. The result will be two series of f-values [28] which are quite suitable for showing the dispersion of Hg; in the following, we will use the second series: the other would give approximately 5% lower energy values.

TABLE 4.

λ (Å)	$E_k - E_0$ (Volt)	f_{k0} (I)	f_{k0} (II)
2537	4·88	0·0255	0·0255
1850	6·67	0·713	0·956
1403	8·79	2·266	
1190	10·38		2·590

With these values we obtain from (19):

$$\begin{aligned}
\varepsilon &= -\frac{17600\cdot 10^{-48}}{R^6}\sum_{kk'}\frac{f_{0k}f_{0k'}}{(E_k-E_0)(E_{k'}-E_0)(E_k+E_{k'}-2E_0)}\ \text{Volt}\\
&= -\frac{17600}{R^6 10^{48}}\left[\frac{2.59^2}{2\cdot 10.38^3}+\frac{2\cdot 2.59\cdot 0.956}{10.38\cdot 6.67\cdot 17.05}+\frac{0.956^2}{2\cdot 6.67^3}\right.\\
&\quad\left.+\frac{2\cdot 2.59\cdot 0.0255}{10.38\cdot 4.88\cdot 15.26}+\frac{0.0255^2}{2\cdot 4.88^3}+\frac{2\cdot 0.956\cdot 0.0255}{4.88\cdot 6.67\cdot 11.55}\right]\\
&= -\frac{17600}{R^6 10^{48}}\cdot(0.00300+0.00420+0.00155+0.00017+0.000003\\
&\qquad +0.00013)\\
&= -\frac{159}{R^6 10^{48}}\ \text{Volt.}
\end{aligned}$$

With R = 3.5 Å (gas kinetic diameter of the Hg-atom) we obtain 0.086 volts for the dissociation energy, if we suddenly allow the repulsion forces to become effective. /249

In calculating the dissociation energies of HgA and HgKr we lack dispersion formulas of equal precision for argon and krypton. Here we will rely mainly on the single term dispersion formulas given by Herzfeld and Wolf whose center of gravity in the continuum lies shortly behind the series limit. The corresponding energy difference in volts is called ΔF, its f-value is g and α is the static polarizability; for Hg we will once again use the same f-values as above and will make use of a mixed formula composed of (19) and (21):

$$\begin{aligned}
\varepsilon &= -\frac{1}{R^6}\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^4\frac{g}{\Delta F}\cdot\sum_k\frac{f_{0k}}{(E_k-E_0)(\Delta F+E_k-E_0)}\\
&= -\frac{1}{R^6}\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^2\alpha\Delta F\sum_k\frac{f_{0k}}{(E_k-E_0)(\Delta F+E_k-E_0)}\\
&= -\frac{164}{R^6 10^{24}}\alpha\Delta F\sum_k\frac{f_{0k}}{(E_k-E_0)(\Delta F+E_k-E_0)}\ \text{Volt.}
\end{aligned}$$

With α = $1.63\cdot 10^{-24}$, ΔF = 17.5 volts and the atomic radius 1.47 Å for argon, for the contribution of the attractive forces to the dissociation energy, we obtain:

$$\begin{aligned}
D_{HgA} &= \frac{164}{3.22^6}\cdot 1.63\cdot 17.5\left[\frac{0.0255}{4.88\cdot 22.4}+\frac{0.956}{6.67\cdot 24.2}+\frac{2.59}{10.38\cdot 27.9}\right]\\
&= 0.063\ \text{Volt.}
\end{aligned}$$

In exact correspondence, we calculate with α = $2.46\cdot 10^{-24}$, ΔF = 14.7 volts and atomic radius 1.21 Å for krypton, and we find the dissociation energy of HgKr as 0.075 volts.

Let us contrast the dissociation energies which we have calculated with the experiment values:

TABLE 5.

	D (theor.) in Volt	D (exper.)
Hg_2	0·086	0·06 ± [29,30,31]
$HgKr$	0·075	0·035[32]
HgA.	0·063	0·025[32]

The agreement would be still more markedly improved if the repulsive forces could be used in the calculations; probably the atomic distances which are assumed were also selected a little too small. But there is probably no point in discussing this further. /250

§7. LIMITS OF VALIDITY

Finally it should be mentioned that the attraction Formulas (6) and (19) cannot be used with complete freedom. For example, we might otherwise come to the conclusion that the chemical bond of H_2 should be viewed as a van der Waals bond, for from $\alpha = 0.66 \cdot 10^{-24}$, $h\nu = 13.5$ volts, $R_0 = 0.75$ Å we can calculate:

$$\varepsilon = \frac{3}{4} \cdot \frac{0{\cdot}66^2 \cdot 13{\cdot}5}{0{\cdot}75^6} = 24{\cdot}6 \text{ Volt.}$$

This would be about six times the binding energy of H_2. We have already pointed out that the operation with a polarizability α is only sensible at distances R for which $R^3 \gg \alpha$. Here, however, $R^3 = 0.64\ \alpha$. If two systems should approach one another above the boundary distance mentioned, they would undergo more or less suddenly a very considerable internal reconstruction of the electron paths and would tear one another apart by polarization. This is no longer taken into account by our approximation formulas. Quite a long time ago, Herzfeld [33] pointed out that in solid bodies the metallic and nonmetallic states are separated by this boundary distance. This also limits the range of applicability of the theory given here. In the case of chemically bound H_2, the atoms are so close together that their "natural" volumes, characterized by α, penetrate one another mutually, so to speak. For checking the applications which we have listed here, we have assembled the quotients $\frac{\alpha}{R_0^3}$:

TABLE 6.

	HCl	HBr	HJ	A	N_2	O_2	Cl_2	CO	CO_2	CH_4	NO	Hg	H
$\frac{\alpha}{R_0^3}$	0·047	0·051	0·035	0·032	0·027	0·030	0·061	0·024	0·046	0·039	0·035	0·13	1·56

We see that our considerations are always within the limits /251 given; $\frac{\alpha}{R^3}$ is the defect parameter of our expansions, and actually a value which is small relative to 1. Hg, with $\frac{\alpha}{R^3} = 0.13$, may already lie very close to the limit of admissibility. The attraction forces calculated above, which were found for Hg_2, HgA, HgKr in the correct order of magnitude, remarkably do not suffice to determine the critical data of Hg. This may have a direct relationship to the fact that Hg is conductive, which shows that the rearrangement of the electron structure (mentioned above) is fulfilled in liquid mercury, if not in the Hg_2-molecule.

Another limitation to our consideration comes from the necessity of taking into account in complex molecules (carbon chains, etc.) the differential attraction ability of the individual molecular ranges. It is clear that it is most likely in molecules as simple as those with which we have been dealing so far, that the ideal of pure force centers can come half-way close to reality. In our work, moreover, we have been able to limit ourselves to a consideration of only the short period terms of the interaction. In highly dipolar substances, especially those with relatively low polarizability (H_2O, NH_3, NaCl, etc.) as well as spatially extensive molecules, the slow periodic (rotation) terms, or those static terms which come from the latter with conversion of rotation into libration, make a considerable contribution, one which is moreover dependent upon temperature and can no longer be ignored; it agrees completely with the familiar static effects of those charge distributions, primarily the so-called Keesom directional effect (see § 2 under "In the second place..."). However, I should like to avoid going into such details here.

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